

**THE TRANSPOSITION OF ESTERS AND THE
INTERDEPENDENCE OF LIMITS**

DISSERTATION

Submitted to the Board of University Studies of The
Johns Hopkins University in conformity with
the requirements for the degree of
Doctor of Philosophy.

By
PAUL D. MARKEL,
Baltimore, Maryland,
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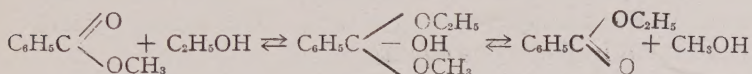
ACKNOWLEDGMENT

This investigation was suggested and carried out under the direction of Dr. E. Emmet Reid and to him the author wishes to express his appreciation and sincere thanks for the assistance so generously given.

The author also wishes to express his gratitude and sincere thanks to Professors Morse and Remsen, Associate Professors Lovelace and Frazer, Collegiate Professors Gilpin and Swartz, and to the late Professor Jones for their valuable instruction and assistance during his University course.

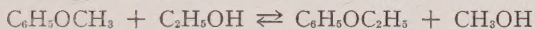
INTRODUCTION

The transposition of esters is commonly regarded as taking place according to the views of Claisen.¹

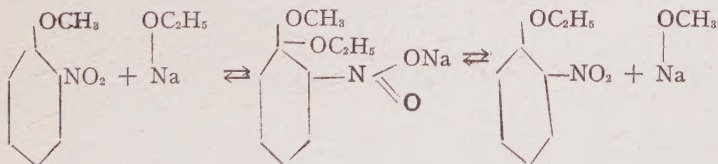


This explanation regards the $> \text{C} = \text{O}$ group as an essential factor in the change, and in the absence of this group this transposition would not be expected to take place.

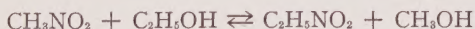
Such transpositions have not been observed in phenol ethers as



but it seemed worth while to try this reaction under influence of strong catalysts and high temperatures to make sure. According to Blanksma² this reaction does actually take place with sodium ethylate as catalyst when the phenol ring contains a nitro group in the ortho or para position. This may be explained in harmony with current views as to tautomeric changes of similar nitro compounds, by assuming the quinone structure for the intermediate compounds.



Some trials have also been made of the possible reaction

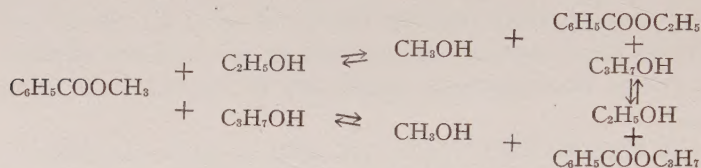


¹ Ber. 20, 646.

² Chem. Weekblad 6, 313.

In this case the methyl is joined directly to the nitrogen and it is not to be expected that transposition should take place. It is well known that the nitrites react readily in this way.

The main part of the work consists in a further quantitative study of the interdependence of limits as exemplified in the transposition of esters. The transpositions represented in the triple equation



have been studied quantitatively at 220° without catalyst and at 100° in presence of very small amounts of the sodium alcoholates. The interest in this was to find whether any one of these equilibria can be calculated from the other two and also whether all three of these equilibria can be predicted from the esterification limits found from the alcoholysis with the free acid. This part of the work is an extension of the work previously done in this Laboratory [Am. Chem. J. 45, 479 (1911)] in which it was shown that the equilibrium between ethyl benzoate and methyl alcohol and methyl benzoate and ethyl alcohol can be so calculated.

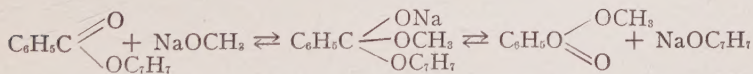
HISTORICAL

Friedel and Crafts³ heated numerous mixtures of alcohols and esters and found that when ethyl acetate is heated with amyl alcohol, amyl acetate and ethyl alcohol are formed. They find the reaction reversible. They also observe that those esters which are saponified most readily are also transformed must readily by alcohols.

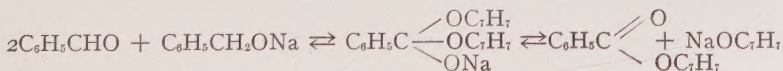
Rose⁴ finds that in the case of etherial carbonates, the higher alcohols replace the lower alcohols more readily than the reverse. Alcohols of higher molecular weight can displace those of lower molecular weight almost entirely but the converse reaction takes place only to a limited extent.

Haller,⁵ Berthelot⁶ and Madinavertia⁷ all effect the displacement of glycerol and other alcohols from various fats, waxes, and esters of simple primary and secondary alcohols using hydrochloric acid as catalyst.

Claisen⁸ heated on the water bath benzyl benzoate with methyl alcohol and methyl benzoate with benzyl alcohol but got no reaction in either case. When he added sodium methylate to the former mixture and sodium benzyolate to the latter, the mixtures solidified, and on acidifying with acetic acid, transformations were found to have taken place. These transformations he assumed had taken place through the formation of the other compounds according to the scheme:



In the formation of benzyl benzoate from benzaldehyde, which he considered as taking place:



3 Ann. 130, 198. Ibid., 133, 207.

4 Ann. 205, 240 (1880).

5 Compt. rend. 143, 657 (1906).

6 Ann. Chem. Phys. (3) 41, 216 (1854).

7 Ann. Soc. Espanola Fisica. Quimica 12, 426 (1914).

8 Ber. 20, 646.

he noted that small amounts of sodium benzylate, since it is regenerated in the reaction, might transform an indefinite amount of the benzaldehyde.

Seelig⁹ attempted to prepare benzyl acetate by heating benzyl chloride and potassium acetate with ethyl alcohol in sealed tubes but obtained ethyl acetate in considerable quantities especially at higher temperatures. He thought that the ethyl acetate was formed by the action of free acetic acid upon the alcohol.

Bertoni¹⁰ found that when amyl nitrite is heated with methyl or ethyl alcohol, double decomposition takes place with formation of methyl or ethyl nitrite and liberation of amyl alcohol.

Bertoni and Truffi¹¹ also working with the nitrites find that there is a regular decrease in transformation with increase in molecular weight of the alcohol.

Patterson and Dickinson¹² find that 90% of methyl tartrate is transformed into the ethyl ester by boiling with ethyl alcohol saturated with hydrogen chloride while in the reverse reaction only 87% is transformed under the same conditions. The amount of each ester present is determined polarimetrically after removal of alcohol and HCl.

Bachmann¹³ in order to identify his product $C_2H_4Cl(OC_2H_5)$ obtained by treatment of diethyl acetal $C_2H_4(OC_2H_5)_2$ with phosphorus pentachloride, allows it to react with sodium methylate. He finds that one alkyl radicle has been replaced by heating with an excess of another alcohol and that while the more complex radicle is replaced by the less complex radicle, the reverse reaction occurs only to a very slight extent.

Peters¹⁴ finds that transformations of the aceto acetates takes place readily with the alcohols as solvents, especially in the presence of small quantities of the alcoholate. In the replacement of a lower by a higher alkyl

9 J. prakt. Chem. (2), 39, 157.

10 Gazz. chim. ital. 12, 435 (1882).

11 Gazz. chim. ital. 14, 23.

12 J. Chem. Soc. 79, 280 (1901).

13 Ann. 218, 38 (1883).

14 Ber. 20, 3318 (1887).

group they find that the reaction is much more complete than in the reverse case.

Conrad and Epstein¹⁵ also find that these transformations take place readily with the aceto acetates and suggest it as a convenient method of preparing the more difficulty prepared acetoacetates from those obtained more readily by the usual method.

Leuchs and Theodorescu¹⁶ find that a solution of ammonia in methyl alcohol will completely transform diethylphloroglucinoldicarboxylate into the dimethyl ester $(\text{HO})_3 \text{C}_6\text{H}(\text{COOCH}_3)_2$, and that this can be converted back into the ethyl ester by the action of ethyl alcohol. They are also able to transform diethylmalonate into the dimethyl ester by the action of ammonia dissolved in methyl alcohol. None of these transformations could be effected, however, without the ammonia.

Henriques¹⁷ studied the transformation of various glycerides in alcoholic solution using sodium ethylate as catalyst and showed that with as little as 15% of the alkali necessary for their saponification, the glycerides are completely transformed into the corresponding ethyl esters.

Kuntze¹⁸ shows that ethers of certain cyclic pseudo-ammonium bases react on warming with alcohols with transposition of their alkyl groups, and Decker¹⁹ offers an explanation of the reaction.

Gadamer²⁰ also offers an explanation in the formation of an intermediate aldehyde alcoholate.

Johnson and Guest²¹ work with some closely related straight chain compounds, the ether-thioureas $\text{RNHCSNHCH}_2\text{OR}'$ and find that in every case the thio-urea reacted with the alcohol on warming with replacement of the alkyl group. They also find the reactions

¹⁵ Ber. 20, 3052 (1887).

¹⁶ Ber. 43, 1248.

¹⁷ Zeit. angew. Chem. 1898, 338.

¹⁸ Arch. Pharm. 246, 110 (1908).

¹⁹ J. prakt. Chem. 45, 182.

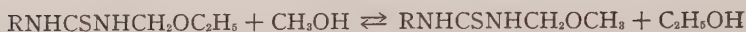
Ber. 25, 3327.

Ber. 33, 1715.

²⁰ Arch. Pharm. 243, 12. Ibid., 246, 89.

²¹ Am. Chem. J. 32, 1279 (1910).

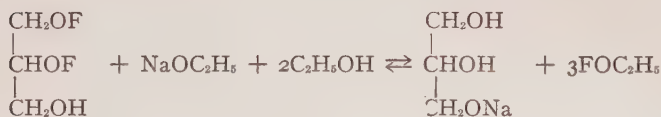
reversible and not influenced by the size of the alkyl groups involved in the change.



They find that Gadamer's theory does not hold but that the simplest explanation for the reaction is the intermediate formation of unstable addition products.

Kommenos²² obtains transformation of esters of acetylenetetra-carboxylic acid, acetoacetic acid, phenyl acetic acid and benzoic acid by means of sodium alcoholates.

Kossel and Kruger²³ show that ethyl salicylate is formed from salol and sodium ethylate and H. Bull²⁴ also effects the saponification of certain esters by means of sodium ethylate according to the following reaction:



when F is a fatty acid radicle.

Goldschmidt²⁵ offers an explanation for the mechanism of this reaction and in a theoretical discussion based upon the work of Henricque²⁶ proposes that the glycerine esters

ionize into RO^- and OCR^+ , the latter then reacts with RO^- of the alcoholate to form a less dissociated ester. The saponification as noted by Henricque is then explained through the formation of some free acylbase $\text{R}-\text{C} \equiv$

O.OH due to hydrolysis of the esters. This then undergoes an intramolecular transformation into the ordinary form of the acid $\text{RC}(=\text{O})\text{OH}$, the transformation being greatly accelerated by the presence of the base KOH.

Reid²⁷ has shown that in the formation of the interme-

²² Monatsh. 31, 111 (1910); Ibid., 31, 687 (1910); Ibid., 32, 77 (1911).

²³ Zeit. physiol. Chem. 15, 321 (1891).

²⁴ Chem. Zeitung 24, 814 (1900).

²⁵ Zeit. Elektroch. 10, 221 (1910).

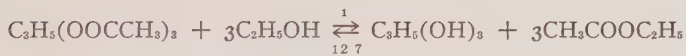
²⁶ Zeit. angew. Chem. 1898, 338.

²⁷ Am. Chem. J., 43, 489 (1910).

diate addition product according to Henry's hypothesis²⁸ for esterification, mercaptan adds to an acid as H— and —SC₂H₅ and not as HS— and —C₂H₅. He concludes that alcohols may or may not add in an analogous manner.

Purdie²⁹ and co-workers obtained numerous examples of transformations. They find that the reaction takes place with esters of fumaric, maleic, oxalic, cinnamic and acetic acids and the best yields are obtained with small amounts of sodium alcoholate and low temperature. They find that a variety of substances will act as catalysts. With the exception of Me, the more complex radicles have a greater affinity for the acids than the less complex radicles, Me falling between Et and Am.

Much quantitative work on the transposition of esters, using sodium alcoholates as catalysts has been done by Kremann³⁰ and Pfannl.³¹ The former worked mainly with polyacetates, particularly triacetin, and finally came to the conclusion that a dynamic equilibrium exists according to



His analytical method was to distill off the ethyl acetate into an excess of standard alkali, the excess of which was subsequently titrated back. The non-volatile triacetin remaining in the distillation flask was likewise determined by saponification. He found the backward velocity in the above reaction to be 12.7 times faster than the forward velocity, the individual determinations running from 7.7 to 17.3. He found a proportionality although not direct, between the velocity of ethyl acetate formation and the amount of NaOH used as catalyst, when less than 5, 6 and 7% of the amount of alkali neces-

²⁸ Ber. 10, 2041.

²⁹ J. Chem. Soc. 47, 855 (1885). Ibid., 51, 627 (1887); Ibid., 53, 391 (1888).

Ber. 20, 1554 (1887).

³⁰ Monatsh 26, 783 (1905). Ibid., 29, 23 (1908).

³¹ Ibid., 31, 301 (1910).

sary for complete saponification of glycoldiacetate, triacetin, and mannite hexacetate was used.

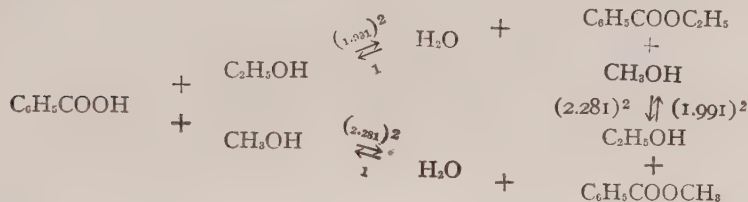
Without catalyst he obtains considerable transformation but attributes the variations in his results to the unequal catalytic influence of the glass walls. All his results point towards the alkali being a true catalyst. With certain complex acids he considered the possibility of steric hindrance to the ester formation. Sudborough has shown that there is such hindrance in the case of doubly ortho-substituted acids.

Pfannl obtained general transformations with the esters with which he worked and in all cases showed that the reactions are reversible. He alternately replaced Me, Et and Pr groups in the terephthalic, benzoic, and oxalic esters by simply dissolving the ester in at least ten parts of the alcohol whose alkyl was wished to be introduced, adding a calculated amount of sodium or potassium alcoholate, and allowing the whole to stand in the cold for definite lengths of time. In every case but one he got quantitative transformations.

He also gains some insight into the velocity of the reaction and shows in a rough way that the velocity is proportional to the amount of alkali present. He is able to do this by taking advantage of the fact that methyl terephthalate is far more insoluble in methyl alcohol than the corresponding diethyl or dipropyl esters. He obtains no transformation in the absence of the alkali. He does not regard the alkali as being a catalyst but adopts the explanation of Claisen for the formation of an intermediate compound.

Reid³² investigated the reaction between ethyl benzoate and methyl alcohol and between methyl benzoate and ethyl alcohol quantitatively, with sodium alkylates and with hydrogen chloride as catalysts and at high temperatures without catalysts, to find the equilibrium point, and, more particularly, to find whether the position of this equilibrium point can be calculated from the limits

of esterification for the two alcohols, as represented in the triple reaction diagram



The numbers were calculated from Menshutkin's limits for the alcohols with acetic acid. In Reid's work the calculation of results was not carried out consistently according to this formulation but the work shows that the equilibrium is reached from either end and that the equilibrium point is located substantially at the place predicted from the esterification limits of the two alcohols.

Kolhatkar³³ studied the action of Me, Et, Pr, iso-Bu and iso-Am alcohols upon the esters of acetic, propionic, butyric, benzoic, monochloracetic, and trichloracetic acids by allowing the reactions to take place in a dilatometer. With a large excess of alcohol (20 molecules) and a constant amount of catalyst (HCl) he gets good constants for a monomolecular reaction.

The dilatometer (50-70 cc.) was filled with alcohol, ester, and catalyst in known proportions and after thirty minutes, which was necessary for temperature equilibrium to be established, the first reading was taken and then at suitable intervals after this. Equilibrium was reached when about 96% of the ester was transformed.

The dilatometer was allowed to remain in the thermostat often for more than a week after the action due to alcoholysis was completed in order to determine the slight correction factor due to the expansion produced by the union of alcohol and hydrochloric acid.

He shows that the rate of transformation by hydrochloric acid decreases as the molecular weight of the acid

increases and "that the relative affinities of the Me and Et groups towards an acyl group are to a certain extent independent of the nature of the acyl group." From the alcoholysis of the acetates, he calculates that the relative activities of the alkyl groups are: Me 100; Et 28; Pr 19; iso-Pr 34; iso-Bu 16; and iso-Am 17.

MATERIALS

Methyl Benzoate and Ethyl Benzoate.—These esters were prepared by heating benzoic acid with the alcohol in the presence of a small amount of concentrated sulphuric acid. The product was carefully purified and fractionally distilled through a short Hempel tube. Practically all of both esters distilled over at a temperature not varying more than 0.1° .

The methyl benzoate boiled at 195.8° 746.6 mm. and had a density of 1.08737 25/25. The ethyl benzoate boiled at 208° and had a density of 1.04540 25/25.

Propyl Benzoate.—A large portion of this ester was made by heating benzoyl chloride with propyl alcohol. The product was shaken with ammonia several times, carefully purified, and finally distilled through a short Hempel tube. The fraction which came over between 228° and 228.5° was used. d. 1.02162 25/25. Some of this ester was also prepared by heating the alcohol and acid in the presence of a small quantity of concentrated sulphuric acid.

Propyl and Ethyl Alcohols.—The ordinary commercial alcohol was refluxed for several days with fresh portions of lime and finally distilled slowly, care being taken to protect the alcohol at all times from the air by calcium chloride-soda lime tubes.

The propyl alcohol had a density of 0.80256 25/25.

The ethyl alcohol had a density of 0.78774 25/25 which according to Circular No. 19 of the Bureau of Standards corresponds to 99.92% pure.

*Methyl Alcohol.*³⁴—Commercial methyl alcohol was refluxed with lime several days, then with anhydrous copper sulphate for about three days, and finally with metallic calcium for several days. This alcohol had a density of 0.79580 25/4 which according to Bureau of Standards' Circular No. 19 corresponds to 99.95% pure.

34 For this I am indebted to Mr. B. B. Wroth of this laboratory.

THE FURNACE

An electric furnace (Fig. I) similar to the one built by Pratt & Reid (J. Am. Chem. Soc. 37, 1934) was con-

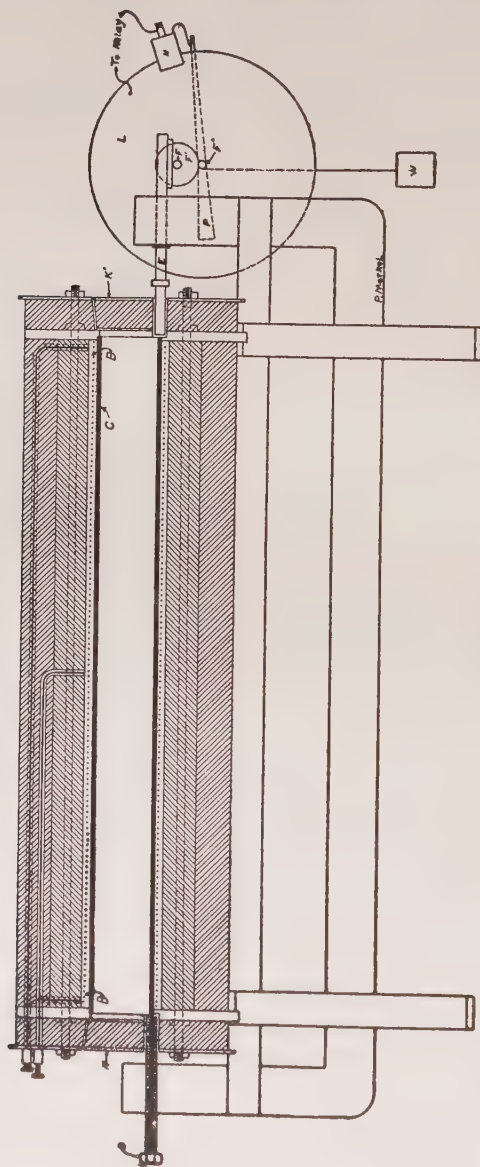


FIGURE I.

structed with certain improvements, however, which gave a much greater accuracy in temperature control.

A copper tube which has a greater temperature coefficient of expansion, was used instead of the brass one, C, and alundum cores in place of porcelain ones, B.B. Both of these have a much greater heat conductivity than the ones used by Pratt and Reid and the "lag" is accordingly greatly reduced.

The alundum cores after being wound with the resistance wire were covered with a thick coat of alundum cement which protects the wires and adds greatly to the life of the furnace.

The ends of the furnace were insulated by 1" asbestos boards and asbestos plugs, K.K'. When the plugs were removed, the furnace could be easily filled by slightly elevating one end so that the tubes could clear the projecting frame. The whole was so arranged that the core and insulation could be entirely removed from the frame after the set screw, D, was removed.

Instead of multiplying the expansion of the metal tube by a system of levers, a series of cogs, F, F', F'' was employed, a brass pointer, P, which moved over the face of a dial, L, being fastened to the smallest cog wheel. A strong coil spring at E keeps the whole system tight up against the set screw, D, and any lost motion in the cogs is eliminated by suspending a 100 g. weight to the drum of the pointer. In this way the pressure against the cogs is always in one direction.

The pointer as it moves over the face of the dial, due to the expansion of the copper tube on heating, comes in contact with a strip of spring brass fastened to a block of hard rubber, H, and in this way a current is made through the relay, the heating current is broken, and the furnace cools until the pointer drops slightly opening the relay current.

At the points of contact between the spring brass and the pointer, strips of platinum foil were soldered.

After the dial had been calibrated, the furnace while at room temperature could be easily set for any temperature desired and after reaching this temperature it remained constant within about one degree for weeks at a time.

PROCEDURE

Glass tubes 360 x 13 mm. were washed with chromic acid, filled with a dilute solution of hydrochloric acid and allowed to stand in boiling water for one hour. They were then washed, filled with distilled water, and allowed to stand in boiling water for another hour, after which they were washed with distilled water, alcohol and finally ether, the last being removed by heating the tubes with a Bunsen burner and aspirating air through until they had become only moderately warm. They were then reheated and cooled as before, after which they were drawn down to a narrow neck.

The tube was weighed and the ester introduced by means of a pipette whose delivering end was small enough to pass through the drawn down neck of the tube. From the weight of the ester, the equivalent amount of alcohol was calculated and either one-half, one, one and one-half, or two molecules of the alcohol were then introduced in a similar manner, the tube sealed, and after cooling, weighed.

Four of these tubes, which was the capacity of the furnace were heated at 220° for varying lengths of time and after cooling were ready for analysis.

Five mixtures of methyl and ethyl esters were prepared and their density taken. On plotting these densities against the percentage of methyl ester (Fig. II) it was found that the values fell slightly below the straight line joining the densities of the pure esters. Accordingly, the composition of the reaction mixture after purification was determined by interpolation of its density with the densities of the five known mixtures of the esters as given in Tables I, II and III.

Numerous experiments were performed in an attempt to free mixtures of the two esters from benzoic acid, water, and the two corresponding alcohols without altering the relative proportion of the two esters present but

in every case it was found that the final density was appreciably lower than the original density of the pure esters before the treatment.

Accordingly a slight correction factor had to be intro-

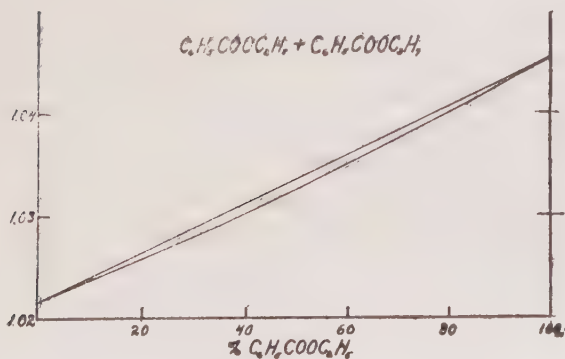
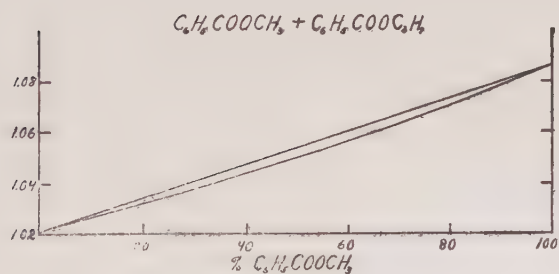
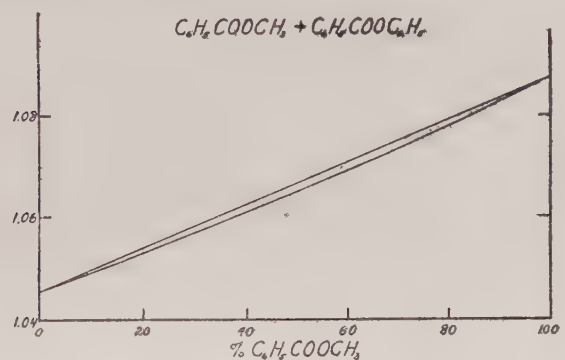


FIGURE II.

duced and its value was carefully determined by submitting a number of samples to the following treatment, which was found to give the best results.

The density was taken of a known mixture of methyl and ethyl esters and after addition of about two molecules of methyl alcohol and ethyl alcohol as well as several milligrams of benzoic acid, the mixture was placed in a separatory funnel, and an equal volume of water added. The funnel was then shaken in a shaking machine for ten minutes and as soon as the two layers had formed distinctly, the esters were run off and shaken again for ten minutes with a fresh quantity of water. They were next shaken with an equal volume of 5% potassium carbonate solution and then with an equal volume of pure water, after which they were shaken twice with $1/2$ volume of water. The esters were then run off with as little water as possible into a long narrow tube which was then placed in boiling water and a rapid stream of dry hydrogen issuing from a fine capillary tube was passed through for one hour, after which the density was taken. In order to remove propyl alcohol, ethyl alcohol, benzoic acid and water from mixtures of the propyl ester and ethyl ester the mixture was shaken three times, ten minutes each time, with equal volumes of water, once with an equal volume of 5% potassium carbonate solution, twice with equal volumes of water and finally six times with one-half volumes of water. Dry hydrogen was then passed through as before and the density taken.

By a series of experiments it was found that in the removal of methyl and ethyl alcohols from a mixture of the two corresponding esters according to this treatment, the density had decreased 0.0002 and for the removal of propyl and ethyl alcohols from their corresponding esters the density had decreased 0.0003.

The reaction mixtures after being heated were put through the treatment necessary for the removal of the alcohols present and the proper correction factor added to the final density.

The densities were taken with pycnometers such as de-

scribed by Jones and Bingham³⁵ as well as with those as described by Davis and Pratt.³⁶ Their capacity varied from 4 to 8 c. c. the larger ones being used almost exclusively.

All the densities were taken at 25° and compared with water at the same temperature, no correction being made for air displacement.

The pycnometers were allowed to remain in a 25° thermostat whose temperatures seldom varied more than 0.003° from the mean, for at least 45 minutes and with a window suitably arranged, they were then set without moving them at all from their position. After cleansing, they were allowed to stand in the balance case at least one-half hour before weighing. Consecutive densities were taken with different pycnometers until an agreement of 2 or 3 units in the fifth place was obtained, more than two determinations being rarely necessary.

35 Am. Chem. J., 34, 495.

36 J. Am. Chem. Soc., 37, 1199.

TABLE I.

Methyl Ester and Ethyl Ester.									
Mol. % Me	0.00	16.46	33.33	50.00	66.11	83.35	100.00		
Density	1.04542	1.05161	1.05802	1.06492	1.07260	1.07947	1.08730		
Diff. in percent	0.00	16.64	16.69	16.67	18.11	15.24	16.65		
Diff. in d.	0.00	0.00619	0.00641	0.00600	0.00768	0.00687	0.00783		
Diff. for 1 percent	0.00	0.000372	0.000384	0.000413	0.000424	0.000450	0.000470		

TABLE II.

Methyl Ester and Propyl Ester.									
Mol. % Me	0.00	24.32	35.51	54.31	66.04	80.19	100.00		
Density	1.02163	1.03458	1.04109	1.05288	1.06082	1.07124	1.08737		
Diff. in percent	0.00	24.32	11.19	18.80	11.73	14.15	19.81		
Diff. in d.	0.00	0.01295	0.00651	0.01179	0.00794	0.01042	0.01613		
Diff. for 1 percent	0.00	0.000531	0.000581	0.000627	0.000676	0.000736	0.000814		

TABLE III.

Ethyl Ester and Propyl Ester.									
Mol. % Et	0.00	20.09	35.29	50.52	61.11	83.31	100.00		
Density	1.02162	1.02592	1.02934	1.03286	1.03542	1.04099	1.04540		
Diff. in percent	0.00	20.09	15.20	15.23	10.59	22.20	16.69		
Diff. in d.	0.00	0.00430	0.00342	0.00352	0.00256	0.00557	0.00443		
Diff. for 1 percent	0.00	0.000214	0.000225	0.000231	0.000241	0.000251	0.000264		

WITH CATALYST

To 10 c. c. of the ester in a drawn-down test tube was added 1 c. c. less than an equivalent amount of alcohol. One c. c. of the corresponding alcoholic solution of sodium was then added, the tube sealed off, and weighed.

Each c. c. of the sodium methylate solution contained 0.00566 g. of sodium; the sodium ethylate solution, 0.00513 g. of sodium; and the sodium propylate solution 0.00439 g. of sodium. These values were found by titra-

N N

tion with 10HCl and $10\text{Ba}(\text{OH})_2$.

The weight of the ester used was taken as also the weight of the alcohol and alcoholate solution, the weight of the sodium present in 1 c. c. of the alcoholate being subtracted from the weight of the alcohol and alcoholate to obtain the weight of the alcohol present.

The tubes were allowed to stand in a 25° thermostat for eight days and after analysis of two series, the remaining tubes were placed in 1" x 6" iron pipes closed at one end, covered with kerosene, and allowed to stand in boiling water for varying lengths of time.

In the analysis, the contents of the tubes were first poured into an equal volume of a saturated solution of sodium bicarbonate and shaken for ten minutes. They were then put through the same treatment according to the alcohols present, as when the alcoholates were absent excepting that the washing with potassium carbonate was omitted.

CALCULATION OF RESULTS

Since, according to the usual reasoning in the consideration of reversible reactions, when we have



the amount of RCOOR'' formed in a unit of time is equal to $(\text{RCOOR}') (\text{R}''\text{OH}) K$, and the amount decomposed in the same unit of time is equal to $(\text{RCOOR}'') (\text{R}'\text{OH}) K'$ (the formulae in parenthesis representing concentrations), and since, at equilibrium these opposing velocities are equal, we have:

$$\frac{(\text{RCOOR}') (\text{R}''\text{OH})}{(\text{RCOOR}'') (\text{R}'\text{OH})} = \frac{K'}{K} = r$$

and if (RCOOR') is equal to $(\text{R}''\text{OH})$ then

$$\frac{\text{Amount of mixture untransformed}}{\text{Amount of mixture transformed}} = \frac{\sqrt{K'}}{\sqrt{K}} = \sqrt{r}$$

or in percentage, the amount of mixture transformed at the limit $= \frac{100}{\sqrt{r} + 1}$ when equivalent amounts of ester and alcohol are used.

In tabulating the results, the data involved are arranged as follows:

- a. Weight of ester in grams.
- b. Millimoles of ester.
- c. Weight of alcohol in grams.
- d. Millimoles of alcohol.
- e. Density 25/25 of ester after purifying.
- f. Corrected density.
- g. Percentage of methyl ester.
- h. Percentage of ethyl ester.

%. Percentage transposition calculated by formula deduced above for equivalent concentrations of ester and alcohol.

The percentage of methyl or ethyl esters, g or h, present after the reaction is completed is obtained by interpolating the corrected density, f, from Tables I, II and III. Knowing the amount of methyl or ethyl ester present, the amount of propyl ester is readily determined by subtraction. The concentration of the ester formed equals the concentration of the alcohol formed. The original concentration of alcohol, d, minus the concentration of the alcohol formed in the reaction gives the final concentration of the alcohol used.

EXPERIMENTAL

I. About 50 c. c. absolute ethyl alcohol containing a little sodium ethylate were added to 10 c. c. anisol (d_{25}^{25} 0.9941) and the mixture allowed to stand at ordinary temperature for 115 hours. The contents of the tube were then shaken seven times, ten minutes each time, with 50 c. c. portions of brine and then dried over calcium chloride. The density was found to be $0.9922 \frac{25}{25}$. Since by a number of experiments this procedure was found to be satisfactory for the purification of the ether and since the corresponding ethyl ether has a density of $0.9694 \frac{25}{25}$ it was concluded that no formation of the ethyl ether had taken place.

II. A mixture of 5.8 g. anisol with 8.2 g. ethyl alcohol containing a little sodium ethylate was sealed in a test tube, the tube placed in an iron pipe and covered with kerosene, and the cylinder then allowed to stand in boiling water for 15 hours. The contents of the test tube were washed with about 140 c.c. of brine in small portions dried over calcium chloride and the density taken. Since the density was found to be $0.9924 \frac{25}{25}$ it was concluded that no transposition of alkyl groups had taken place.

III. About equal molecular proportions of anisol and ethyl alcohol containing a little sodium ethylate were sealed in a glass tube and kept at 250° for 120 hours. The contents of the tube were then heated in a distilling flask till no more alcohol distilled over below 100° and then washed fifteen times with 5 c. c portions of brine. The density was found to be $0.9938 \frac{25}{25}$ which indicated

that no reaction had taken place under these conditions.

IV. A mixture of 0.6 g. β -naphthol methyl ether with about ten molecules of ethyl alcohol containing a little sodium ethylate was sealed in a glass tube and kept at

100° for 14 hours. After washing the contents well with water, the melting point of the solid was found to be 72° which is the melting point of the pure $C_{10}H_7OCH_3$. Similar negative results were obtained using hydrogen chloride as catalyst and heating at 150° for several days.

V. A mixture of 5.68 g. nitromethane, 7.83 g. ethyl alcohol and a little sodium ethylate was sealed in a test tube and heated at 100° for 18 hours. The contents became colored reddish-brown and a considerable black deposit,³⁷ was formed. Since all of the solution dissolved in the brine, it was concluded that no nitroethane had formed.

VI. About equal quantities of nitromethane and ethyl alcohol containing some hydrogen chloride were sealed in a glass tube and kept at 100° for 20 hours. The most of the alcohol was removed by heating to 80°. The slight residue remaining was washed ten times with equal portions of brine, dried over calcium chloride and the density taken. It was found to be 1.1270_{25}^{25} . Since several mixtures of CH_3NO_2 and C_2H_5OH after being subjected to the same purification treatment gave a density of 1.1292_{25}^{25} and since nitromethane has a density of $1.0528,$ ³⁸ it was concluded that no reaction had taken place.

VII. Equal quantities of nitromethane and ethyl alcohol containing a little sodium ethylate were allowed to stand 22 hours at ordinary temperature. After being washed, the density was found to be 1.1269_{25}^{25} which indicated that no reaction had taken place.

VIII. A solution of nitromethane with about twice as much ethyl alcohol containing a little hydrogen chloride was sealed in a glass tube and kept at 200° for 20 hours. The solution had become brown and a light precipitate had formed. After washing, the solution was fraction-

³⁷ B. 10, 140 (1877).

³⁸ B. 10, 2083.

ally distilled and since all came over below 101° , the boiling point of nitromethane, it was concluded that no nitroethane had formed.

TABLE A— $C_6H_5COOCH_3 + C_2H_5OH$

3 days at 250° .

a	13.688	11.490	11.846	12.245
b	100.60	84.47	87.06	89.99
c	2.370	4.253	7.935	6.052
d	51.48	92.36	172.30	131.41
e	1.08535	1.08447	1.08189	1.08223
f	1.08555	1.08467	1.08209	1.08243
g	96.28	94.41	88.92	89.64
Vr	18.2	17.7	11.6	10.6
%	5.21	5.34	7.91	8.58

TABLE A— $C_6H_5COOCH_3 + C_2H_5OH$.

4 days at 220° .

a	15.510	14.589	10.428	11.163
b	113.99	107.22	76.64	82.04
c	1.486	6.363	6.148	3.328
d	32.27	138.16	133.50	72.26
e	1.07782	1.06606	1.06171	1.06832
f	1.07802	1.06626	1.06191	1.06852
g	80.14	53.16	42.73	58.50
Vr	1.31	1.41	1.23	1.26
%	43.29	41.49	44.74	44.29

Av. Vr = 1.304

TABLE A'— $C_6H_5COOCH_3 + C_2H_5OH$.

10 days at 220° .

a	12.363	11.609	11.823	11.365
b	90.86	85.32	86.89	83.53
c	6.862	8.638	4.415	2.103
d	149.01	187.59	95.88	45.66
e	1.06130	1.05872	1.06548	1.07230
f	1.06150	1.05892	1.06568	1.07250
g	41.75	35.50	51.79	67.88
Vr	1.141	1.151	1.177	1.218
%	46.7	46.5	45.9	45.1

Av. Vr = 1.172

TABLE C— $\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5 + \text{CH}_3\text{OH}$.

12 days at 220°.

a	13.067	12.889	13.299	12.144
b	87.07	85.88	88.61	80.92
c	5.932	3.181	4.366	2.453
d	185.21	99.31	136.32	76.58
e	1.07471	1.06793	1.07112	1.06601
f	1.07491	1.06813	1.07132	1.06621
g	73.24	57.57	65.10	53.04
V r	1.199	1.160	1.170	1.186
%	45.5	46.3	46.0	46.7

Av. V r = 1.179

TABLE B— $\text{C}_6\text{H}_5\text{COOCH}_3 + \text{C}_3\text{H}_7\text{OH}$.

7 days at 220°.

a	12.007	11.783	11.753	11.733
b	88.24	86.60	86.38	86.23
c	5.653	10.381	7.290	2.671
d	94.12	172.84	121.37	44.47
e	1.05034	1.04108	1.04630	1.06194
f	1.05059	1.04133	1.04655	1.06219
g	50.66	35.89	44.22	67.90
V r	1.092	1.088	1.097	1.133
%	47.8	47.9	47.7	46.9

Av. V r = 1.102

TABLE E— $\text{C}_6\text{H}_5\text{COOC}_3\text{H}_7 + \text{CH}_3\text{OH}$.

13 days at 220°.

a	12.267	12.091	12.404	12.640
b	74.75	73.68	75.59	77.03
c	4.982	4.092	2.706	1.625
d	155.53	127.76	84.48	50.75
e	1.05523	1.05402	1.04722	1.04050
f	1.05553	1.05432	1.04752	1.04080
g	58.23	56.44	45.77	35.02
V r	1.358	1.265	1.307	1.279
%	42.4	44.1	43.3	43.9

Av. V r = 1.302

TABLE D— $\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{OH}$.4 days at 220° .

a	11.084	10.885	11.317	12.194
b	73.85	72.53	75.40	81.25
c	6.679	9.532	2.339	4.881
d	111.20	158.70	38.95	81.27
e	1.03375	1.03302	1.03770	1.03231
f	1.03395	1.03322	1.03790	1.03251
h	54.63	52.01	71.00	49.27
$\sqrt{r}$	1.667	1.964	1.384	1.029
%	37.5	33.8	41.9	49.3

TABLE D— $\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{OH}$.12 days at 220° .

a	12.351	12.247	12.298	12.328
b	82.30	81.60	81.94	82.14
c	7.036	5.473	10.088	2.800
d	117.15	91.12	167.96	46.62
e	1.02898	1.03075	1.02641	1.03574
f	1.02928	1.03105	1.02671	1.03604
h	35.03	42.69	23.60	63.58
$\sqrt{r}$	1.248	1.190	1.387	1.013
%	44.5	45.6	41.9	49.7

TABLE F— $\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{OH}$.12 days at 220° .

a	10.692	10.622	11.083	10.938
b	65.16	64.73	67.54	66.65
c	4.510	6.763	1.634	3.100
d	97.93	146.85	35.47	67.31
e	1.03213	1.03447	1.02710	1.02902
f	1.03243	1.03477	1.02740	1.02932
h	48.66	58.43	26.66	35.21
$\sqrt{r}$	1.485	1.432	1.634	1.854
%	40.2	41.1	38.0	35.0

TABLE F— $\text{C}_6\text{H}_5\text{COOC}_3\text{H}_7 + \text{C}_2\text{H}_5\text{OH}$.12 days at 220° .

a	12.082	11.098	12.414	12.309
b	73.62	67.63	75.65	75.01
c	7.011	2.814	4.227	5.099
d	152.24	61.10	91.79	110.73
e	1.03181	1.02755	1.03160	1.03172
f	1.03211	1.02785	1.03190	1.03202
h	47.41	28.84	46.54	47.04
$\sqrt{r}$	1.931	2.574	1.359	1.551
%	34.1	28.0	42.4	39.2

TABLE G— $\text{C}_6\text{H}_5\text{COOCH}_3 + \text{C}_2\text{H}_5\text{OH}$.With Catalyst at 100° .

	A	B
a	10.827	10.870
b	79.57	79.89
c	3.708	3.704
d	80.52	80.43
e	1.06683	1.06696
f	1.06703	1.06716
g	54.97	55.28
Time	22 hrs.	22 hrs.
$\sqrt{r}$	1.234	1.244
%	44.8	45.0

TABLE I— $\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5 + \text{CH}_3\text{OH}$.

	G	H	I
a	10.410	10.401	10.441
b	69.36	69.30	69.57
c	2.234	2.267	2.178
d	69.75	70.84	68.00
e	1.06689	1.06695	1.06658
f	1.06709	1.06715	1.06678
g	55.11	55.26	54.38
Time	41 hrs.	41 hrs.	41 hrs.
$\sqrt{r}$	1.220	1.207	1.223
%	45.0	45.3	45.0

TABLE H— $\text{C}_6\text{H}_5\text{COOCH}_3 + \text{C}_2\text{H}_5\text{OH}$.

	D	E	F
a	10.829	10.843	10.826
b	79.59	79.69	79.57
c	4.785	4.781	4.766
d	79.67	79.60	79.35
e	1.05526	1.05477	1.05566
f	1.0556	1.05500	1.05596
g	58.27	57.44	58.86
Time	60 hrs.	60 hrs.	60 hrs.
V r	1.397	1.348	1.427
%	41.7	42.6	41.2

TABLE L— $\text{C}_6\text{H}_5\text{COOCH}_2\text{H}_7 + \text{CH}_3\text{OH}$.

	M	N	P
a	10.147	10.168	10.184
b	61.83	61.96	62.06
c	2.032	2.022	2.027
d	63.44	63.13	63.28
e	1.04457	1.04712	1.04968
f	1.04487	1.04742	1.04998
g	41.53	45.60	49.69
Time	58 hrs.	58 hrs.	104 hrs.
V r	1.438	1.081	1.032
%	41.0	48.0	49.2

TABLE K— $\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{OH}$.

	J	K	L
a	10.415	10.404	10.451
b	69.40	69.32	69.64
c	4.156	4.188	4.186
d	69.20	69.73	69.70
e	1.03571	1.03623	1.03619
f	1.03601	1.03653	1.03649
h	63.46	65.53	65.37
V r	1.733	1.910	1.889
%	36.6	34.4	34.6

TABLE M— $\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{OH}$.

	R	S	T
a	10.165	10.216	10.146
b	61.94	62.25	61.83
c	2.873	2.873	3.058
d	62.39	62.39	66.41
e	1.02649	1.02679	1.02784
f	1.02680	1.02709	1.02814
h	24.00	25.29	29.96
Vr	3.182	2.959	2.458
%	23.9	25.3	28.9

DISCUSSION OF RESULTS

From the results, as a whole, it appears that all of the reactions are very slow even at 220° . There is considerable irregularity in the results as in some cases equilibrium is reached in comparatively short time while in other mixtures that were heated much longer, it was not reached. It is known that small traces of alkali, present as alkylate, accelerates the reaction enormously. All of the tubes were cleaned with dilute acid but in different tubes there may have been varying amounts of alkali that would be attached by the alcohols at the high temperatures of the experiments.

The fact that the reactions were slow shows the purity of the reacting substances. With those experiments in which the sodium alkylates were used as catalysts, the amounts put in were made very small so as to avoid change of limit due to alteration of concentrations by the catalyst. The amounts used were too small to give rapid transformation. The slowness of the reaction and length of time required for analysis prevented a repetition of the experiments in several of the series. Entirely satisfactory results have been obtained in the case of the reaction of methyl alcohol on ethyl benzoate and ethyl alcohol on methyl benzoate.

In Table A' for the reaction of ethyl alcohol on methyl benzoate we have 46.7, 46.5, 45.9 and 45.1 as percentages of the ethyl ester, at equilibrium. These give $\sqrt{r} = 1.141, 1.151, 1.181$ and 1.22 , as average 1.17 . From the other end by the action of methyl alcohol and ethyl benzoate, in Table C, we have 45.5, 46.3, 46.1 and 45.7 per cent. of ethyl ester at equilibrium and $\sqrt{r} = 1.20, 1.16, 1.17$, and 1.19 , aver. 1.18 . Thus the same equilibrium point is reached from both ends, and we may take $\sqrt{r} = 1.174$ as 46.0% of ethyl ester as very close to the correct result. From Menshutkin's figures for methyl and ethyl alcohol with acetic acid, we have $2.281 \div 1.991 = 1.146$ or 46.6%. These are at 220° without catalyst. At 100° with catalyst, from Table G we have $\sqrt{r} = 1.23$, and 1.24 , average

1.24 as 44.8 and 45.0% while from Table I, from the other end, $\sqrt{r} = 1.22$, 1.21 and 1.22, average 1.22 as 55.0, 54.7 and 55.0%. Here again we have the same equilibrium point reached from both ends, namely: 44.2% as $\sqrt{r}$ 1.23.

There appears to be a slight difference in the equilibrium point at the two different temperatures, 46.0% of ethyl ester at 220° and 44.2% at 100°. It is maintained by some that the esterification limits shift slightly with change of temperature.

The results in the other series do not give reliable information as to the other equilibria as it is not certain that the limits were reached. In the experiments in Table B in which methyl benzoate was heated with propyl alcohol the figures are 47.8, 47.9, 47.7 and 46.9 per cent. of propyl ester, as $\sqrt{r} = 1.09$, 1.09, 1.10 and 1.13, average 1.10. These agree closely with 46.9% and $\sqrt{r} = 1.13$ calculated from Menshutkin's figures but the results for the reverse reaction in Table E are far below the calculated limit.

In Table D when ethyl benzoate was heated with propyl alcohol, the results of the first three which were heated only four days, are low, but the fifth, sixth, and seventh mixtures show too little ethyl ester, the reaction having, apparently, gone past the limit. There must be some error in the results. In all the remaining series, the equilibrium points have not been reached.

In all of the experiments in which the equilibria have been certainly reached, the results are in accordance with the theory and it seems proved that the equilibrium point for the reaction between one alcohol and the ester of another alcohol can be correctly calculated from the esterification limits of the two alcohols in question.

CONCLUSIONS

1. Methyl, ethyl and propyl alcohols displace each other from their benzoates very slowly at 220° without catalysts.

2. They also replace each other at 100° when very small amounts of sodium alkylates are present.

3. Methyl and ethyl alcohol replace each other to nearly the same extent at 100° with sodium alkylate as at 220° without catalyst, though there seems to be a slight difference in the two cases, 44.2% ethyl ester at the limit at 100° and 46.0% at 220°.

4. For the reaction



the forward velocity in $(1.17)^2 = 1.37$ times the backward velocity.

BIOGRAPHY

Paul David Markel was born in Union Bridge, Maryland, on June 21, 1892. He received his early education at Maryland Collegiate Institute at Union Bridge. In 1907 he entered the Preparatory Department of Western Maryland College from which he graduated in 1908. After spending two years at Western Maryland College, he entered Pennsylvania College in 1910 and graduated in 1913, receiving the degree of Bachelor of Science. He entered Johns Hopkins University in 1913 as a graduate student and continued his work in chemistry for three years, making Physical Chemistry his first subordinate and Mineralogy his second subordinate. During the academic year 1914-1915 he held the position of laboratory assistant to Professors Gilpin and Lovelace.

